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[12] Such symmetry is in itself a necessary but not sufficient condition of persistent-complex formation. Direct reactions which could give such a distribution are conceivable though unlikely. One possibility in the present case is that electron transfer can occur rapidly, compared to the time of collision. Thus $C_2H_4^+$ could in effect approach the center of mass from either direction. However, the fact that the distribution is quite unsymmetric at higher energies shows that electron transfer is not fast compared to the collision period. Furthermore, in the system $C_2D_4^+ + C_2H_4$, products of different isotopic composition all show symmetric distributions, a finding which is implausible if the results are a consequence of direct reaction between colliding $C_2D_4 + C_2H_4$ and $C_2D_4 + C_2H_4^+$.

[13] In decomposition of $C_3H_5^+$ most of the kinetic energy is carried by H_2. Thus the velocity vector of the $C_3H_3^+$ should be quite similar to that of $C_3H_5^+$ parent.

Direct Mechanism of Reaction $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$

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Recent crossed-beam experiments have started to provide detailed evidence for the formation of persistent complexes in certain reactions.[1,2] Ion–molecule reactions between $C_2H_4^+$ and C_2H_4 appear, at relative energies of a few electron volts, to be dominated by such intermediates.[2,3] This is not the case for processes such as $Ar^+ + D_2 \rightarrow ArD^+ + D$, even at energies as low as 0.1 eV (center of mass).[4] The question then arises as to whether a persistent complex is formed whenever the composition of the transition state corresponds to that of a stable structure. We report here certain crossed-beam experiments which appear to shed some light on this and other factors which control intermediate complex formation. The reaction $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$ and its perdeutero analog were studied. The putative intermediate complex, $C_2H_7^+$, has been directly observed when produced by certain other reactions[5] and appears to be stable in its ground state. However, prior evidence on whether or not this entity is a persistent complex in this reaction is not definitive.[6,7]

The apparatus EVA[8] was used to produce CH_3^+ by electron bombardment of CH_4. The mass-analyzed beam, variable in energy from 1 to 10 eV, was crossed with a thermal beam of CH_4. Results on velocity and angular spectra of $C_2H_5^+$ are displayed in Fig. 1. As in the previous article,[2] a center-of-mass representation of the velocity-vector diagram in Cartesian space is employed.

It is evident that even at the lowest energies, the distribution has no symmetry about the center of mass

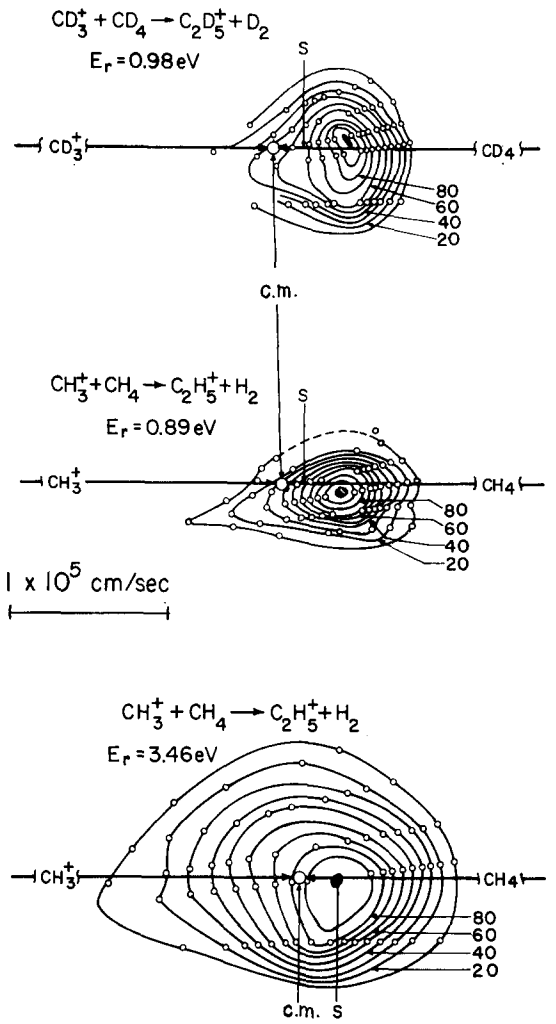

FIG. 1. Velocity-vector diagrams in the c.m. system of angular and velocity distributions of $C_2H_5^+$. Arrows represent center-of-mass velocity vectors of reactants. A vector from c.m. indicates the velocity and direction, with respect to the CH_3^+ vector, of products shown at any given point. Contours show product intensities normalized to 100 for each diagram. *S* indicates the product velocity for the "spectator stripping." [It is noted that at low energies the distribution is actually relatively more forward peaked than at high energies. The same phenomenon was noted for other direct reactions, such as $Ar^+ + D_2 \rightarrow ArD^+ + D$, and has been attributed to an ion-induced-dipole acceleration of the reactants (see Ref. 4).] (Relative energies are indicated.)

but is peaked forward. This shows that there is no dominant contribution by an intermediate persistent complex having a lifetime of more than a few rotations ($\gtrsim 10^{-12}$ sec). The reaction is thus direct despite the fact that "stable" $C_2H_7^+$ can exist.

These findings may be explained by recourse to the simple theory of unimolecular decay. RRK theory[9] provides as an order-of-magnitude estimate of lifetime with respect to decay the expression

$$\tau = 10^{-13}[(E - E^*)/E]^{1-s}. \quad (1)$$

Here E is the total energy available, E^* is the stability (the "well depth") of the species, and s is the number of "active" vibrational modes. E is the sum of the relative

kinetic and internal energies of the reactants and the exoergicity of the process $CH_3^+ + CH_4 \rightarrow C_2H_7^+$. Available thermochemical data indicate the exoergicity to be 0.8–1.2 eV.[10,11] The internal energy of the CH_4 is of the order of 0.1 eV. That of CH_3^+ as formed by the electron bombardment of CH_4 may be estimated to range between 0–3 eV with a mean at 1.0 eV. E^* is the energy required for $C_2H_7^+$ to decompose from its ground state to the minimum energy products, in this case $C_2H_5^+ + H_2$. The quantity ΔE for this process is small and uncertain, in the range 0–0.4 eV.[11] Assuming that the barrier to the reverse recombination is negligible, E^* is then only 0–0.4 eV.

The above considerations indicate that even at the lowest relative energy measured, 0.62 eV, the bracketed quantity in Eq. (1) is between 1 and 0.86. The value s is uncertain but cannot be greater than 21. Hence, τ will be between 10^{-13} and 2×10^{-12} sec depending on the true value of E^*. The actual lifetime is likely to be at the short end of this range since there is scarcely time for complete statistical redistribution of internal energy, and the effective value of s will thus be considerably smaller than maximal. The finding that a persistent complex is not observed now appears reasonable. Even though a $C_2H_7^+$ intermediate of lowest-energy configuration may be formed, it will not usually live long enough to undergo the number of rotations necessary for it to "forget" the direction from which the reactants arrived.

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[10] $\Delta H(C_2H_7^+)$ has been estimated to be "slightly lower than 225 kcal/mole."[5] Other estimation based on the occurrence and nonoccurrence of I–M reactions[6] gives a value $\Delta H(C_2H_7^+) > 216$ kcal/mole.

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Molecular Beam Kinetics: Evidence for Preferred Geometry in Interhalogen Exchange Reactions*

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Halogen atom–molecule exchange reactions have been studied in solution,[1] in photochemical systems,[2,3] and, most recently, in crossed molecular beams.[4–6] These reactions offer an opportunity to look for effects arising from formation of triatomic halogen complexes, which have often been postulated (and occasionally disputed) as intermediates in the mechanism of halogen-atom recombination and other processes.[7] Such complexes have not yet been detected in the gas phase, although the Cl_3 radical has been identified in a matrix-isolation experiment.[8] Evidence that short-range attraction indeed governs the exchange reactions of $Cl + Br_2$ [4–6] and $Br + I_2$ [4] was found in the product angular distributions observed in the molecular beam studies.

Several properties of the trihalogen radicals can be inferred from the experimental findings and simple electronic structure arguments. (1) The bonding is expected[9,10] to resemble that in the negative trihalide ions, which have linear or nearly linear geometry and vibrational force constants corresponding to "half-bonds."[11] The outermost valence electron in X_3 and the outermost two in X_3^- occupy a molecular orbital that is nonbonding or only weakly antibonding in the linear configuration and antibonding in the bent configuration. The infrared spectrum of Cl_3 nicely demonstrates the resemblance to Cl_3^-.[8] (2) Complexes containing iodine are more stable than those containing only bromine or chlorine. The low ionization potential of the I atom favors charge-transfer stabilization. The efficiency of the parent X_2 molecules as catalysts for X atom recombination are consistent with this order of stability.[12–14] From the temperature dependence of the atom recombination rate, the dissociation energy is estimated[12] as 5 kcal/mole for I_3, and roughly 3 and 1 kcal/mole for Br_3 and Cl_3. The form of the wide angle reactive scattering[4] also indicates that the BrI_2 complex is appreciably more stable than $ClBr_2$. (3) For complexes containing

TABLE I. Reaction paths and exothermicity (kilocalories per mole).

Reactants	Intermediate	Products	ΔD_0
Cl+IBr	(a) Cl–I–Br	ClI+Br	8
Cl+BrI	(b) Cl–Br–I	ClBr+I	10
Br+ClI	(c) Br–Cl–I	BrCl+I	3
Br+ICl	(d) Br–I–Cl	BrI+Cl	−8